Utilization of Non-Destructive Tools for In-Situ Determination of Hydrogen Content in Advanced Materials

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Outline

- Introduction

- Common Factor Between Electronic Tools and Hydrogen Measurements

- Non-Destructive Hydrogen Content Sensors
  - Thermoelectric Power Measurements
  - Low Frequency Impedance Measurements

- Results

- Summary

NDE Progress and Challenges

The NDE Community has made impressive advancements in assessment of material defects and increased structural integrity

New Challenges:

- To Assess Material Health
  - - Aging - Properties - Specifications
  - - Stability - Strain State
- To non-destructively characterize material in technical assemblies with electronic, magnetic, and elastic metallography techniques
- To be integrated in agile vertical manufacturing systems
- To rapidly perform real-time testing, data acquisition, and assessment, to qualify materials during manufacturing

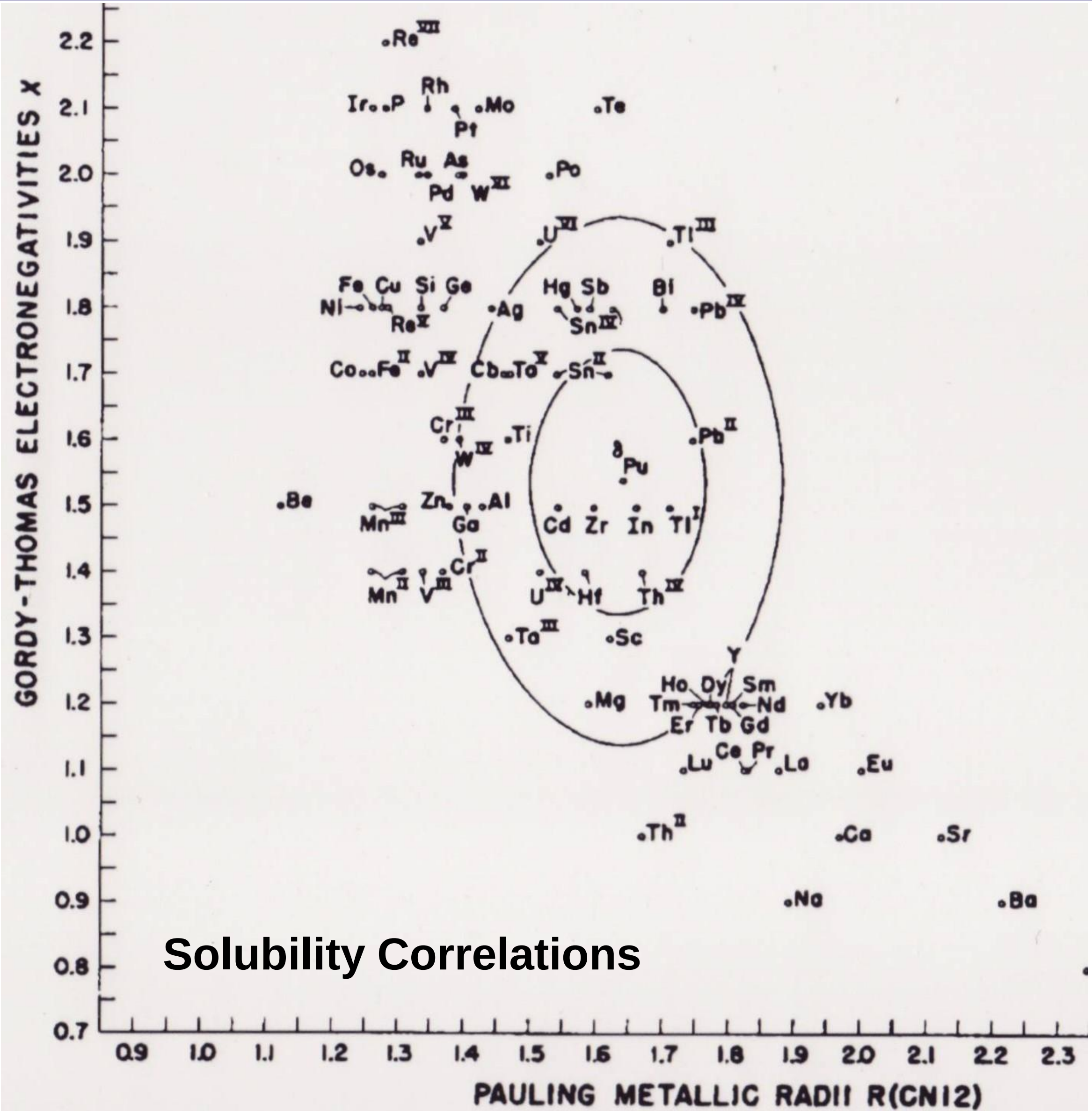
Early Metallurgical Approach

Hume-Rothery

Darken-Gurry

Gschneider

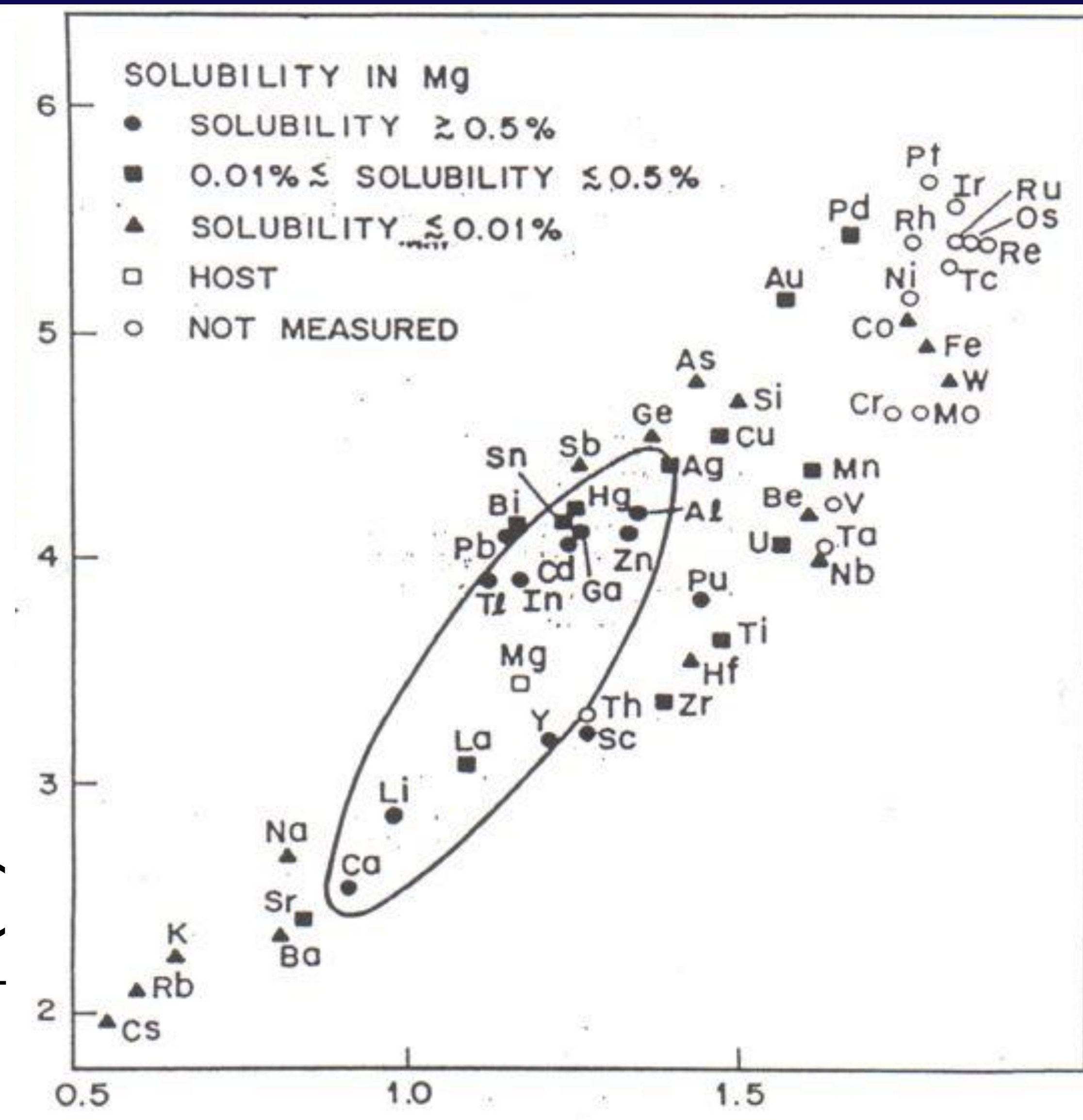
Waber



Early Metallurgical Approach

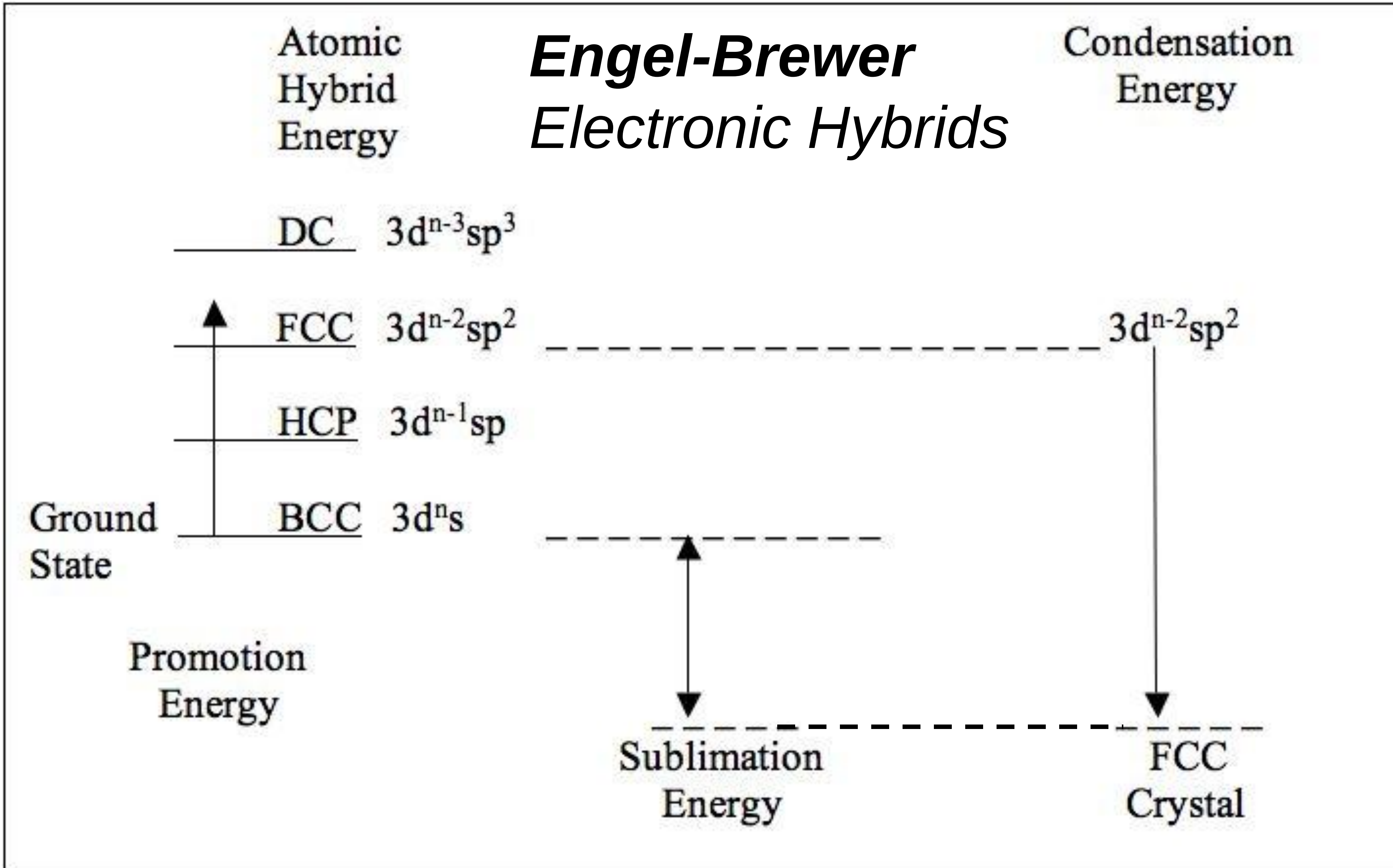
Miedema-Chelikowsky

ϕ^* (eV) Related to the elemental work function



$N_{ws}^{1/3}$ (d.u.) $^{1/3}$ **Related to Bulk Modulus/Vol.**

Early Metallurgical Approach



Electronic Property Crystal Structure Correlation

Brewer

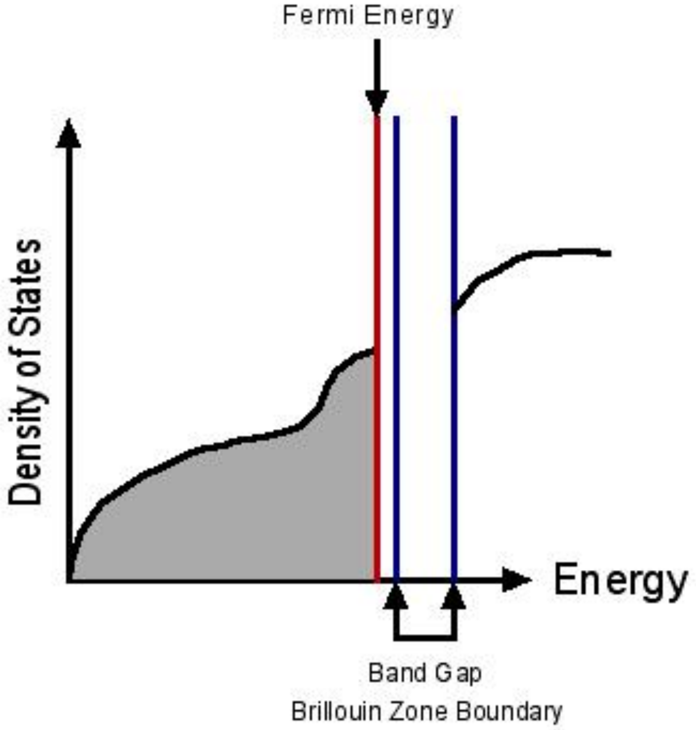
- Consider the number of unpaired s and p electrons

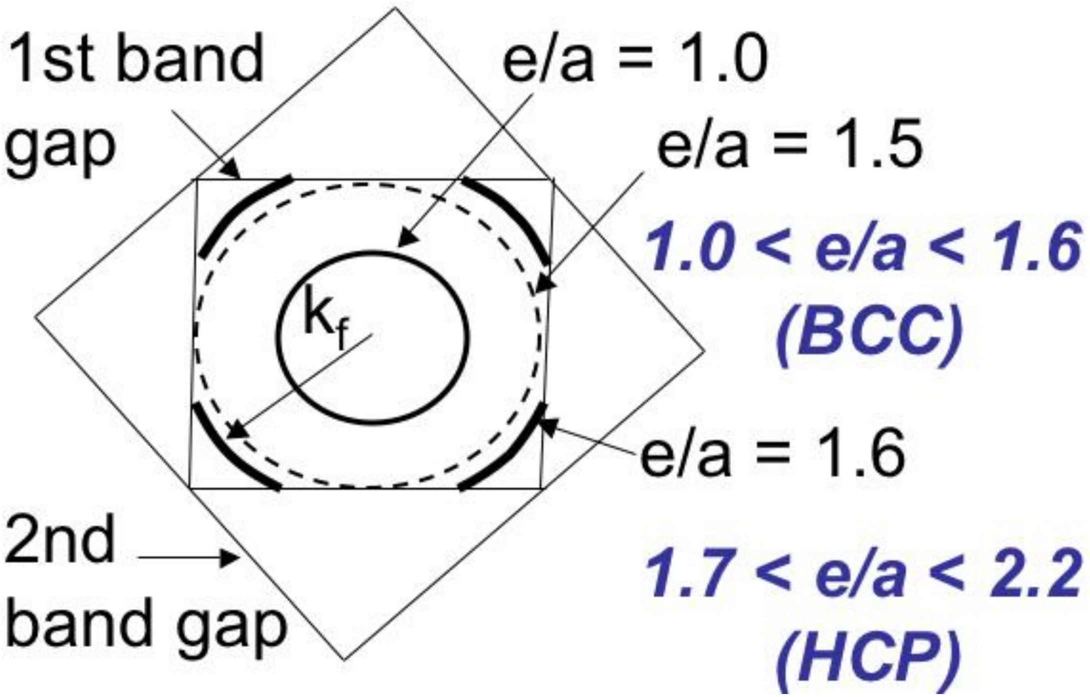
Crystal Structure	Elements e/a ratio	Alloys e/a ratio	Electronic Configuration
BCC	1	< 1.5	$d^n s$
HCP	2	1.7 to 2.1	$d^n sp$
FCC	3	2.5 to 3.0	$d^n sp^2$
Diamond	4	>3.5	$d^n sp^3$

Early Physics Approach

Intro to Wave Mechanics - *Mott and Jones*

- Ziman





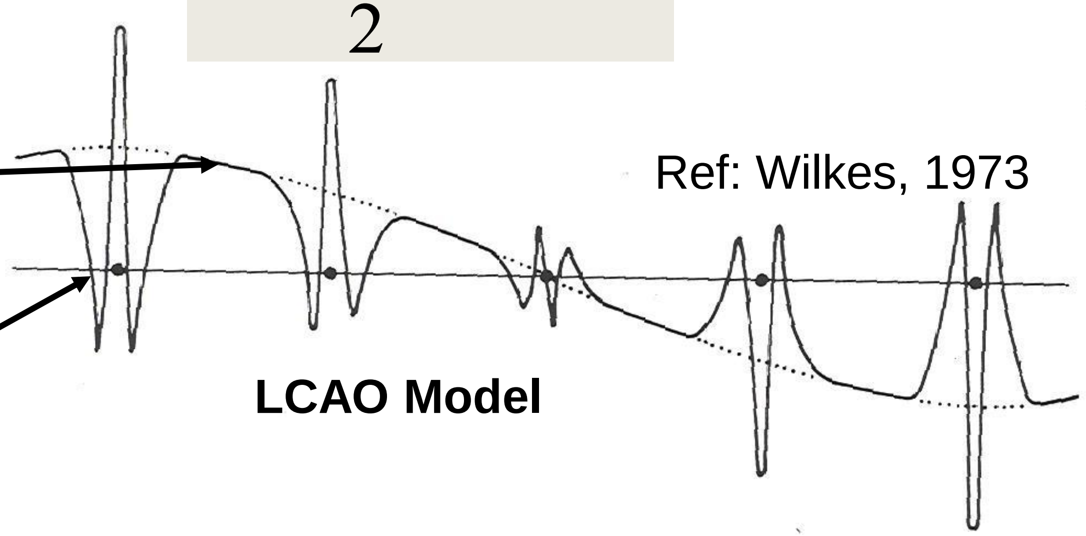
Effective Mass

- Electron wave function is modified by localized potentials

$$E = \frac{1}{2} m v^2 + V$$

- Free Electron Wave (-----)

+ Localized Potential



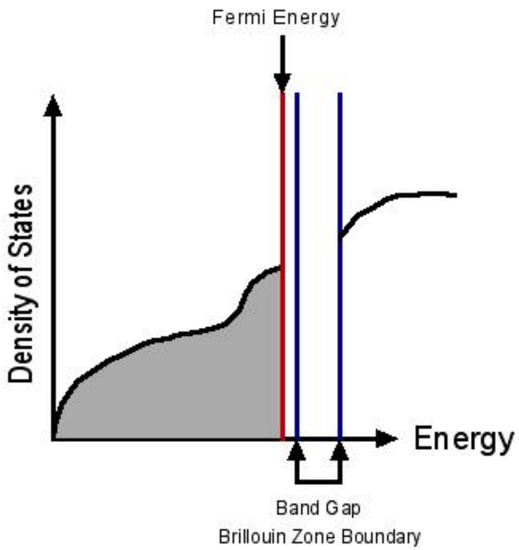
Ref: Wilkes, 1973

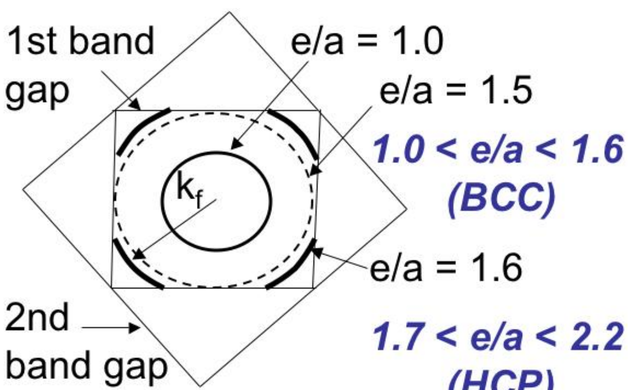
LCAO Model

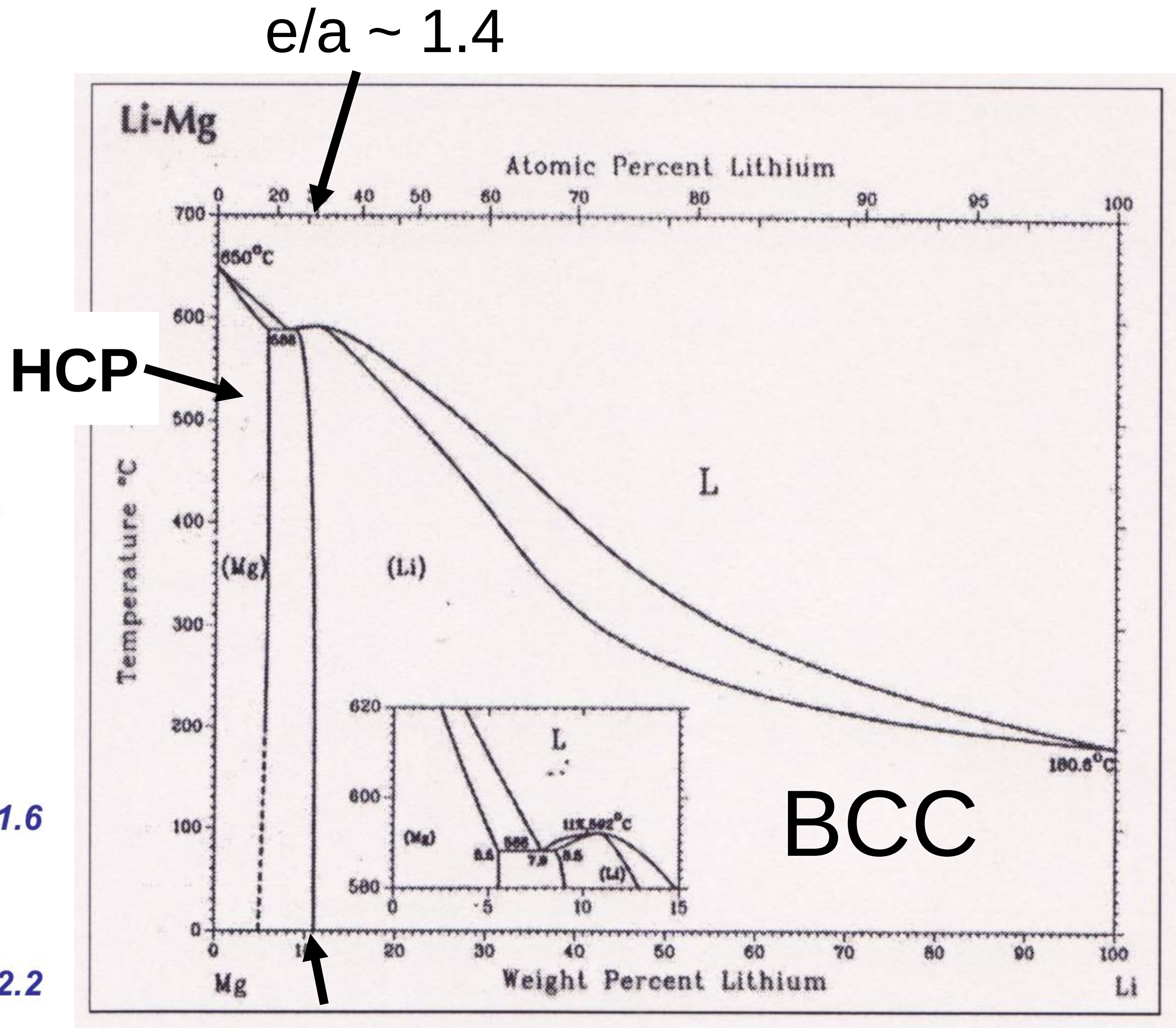
$$E = \frac{1}{2} m v^2 = \frac{P^2}{2m} = \frac{\hbar^2 k^2}{2m_e}$$

$$m_e = \frac{\hbar^2}{\left(d^2E \big/ dk^2\right)}$$

Correlation of Phase Diagram to Electronic Filling of Band Structure

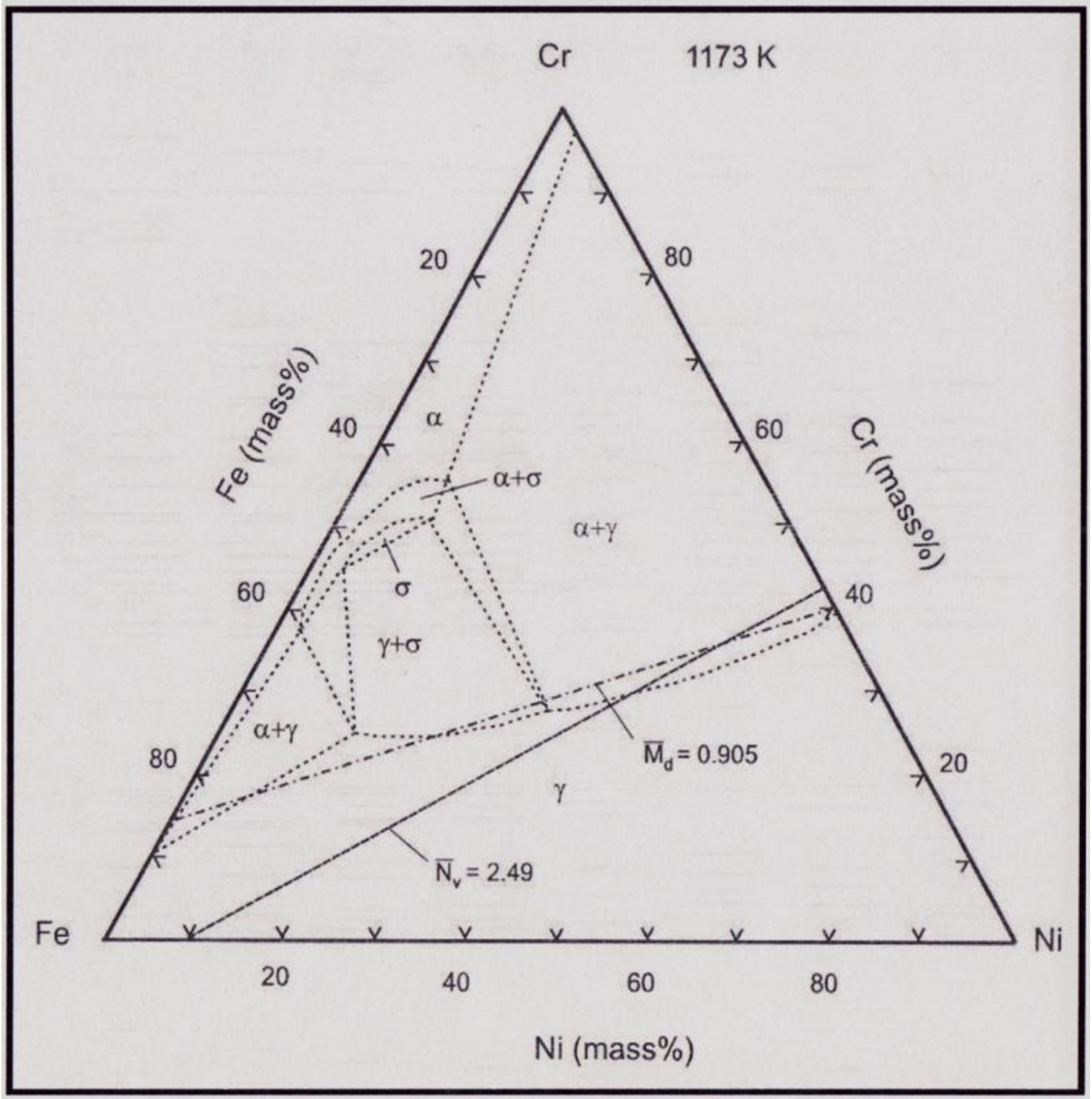




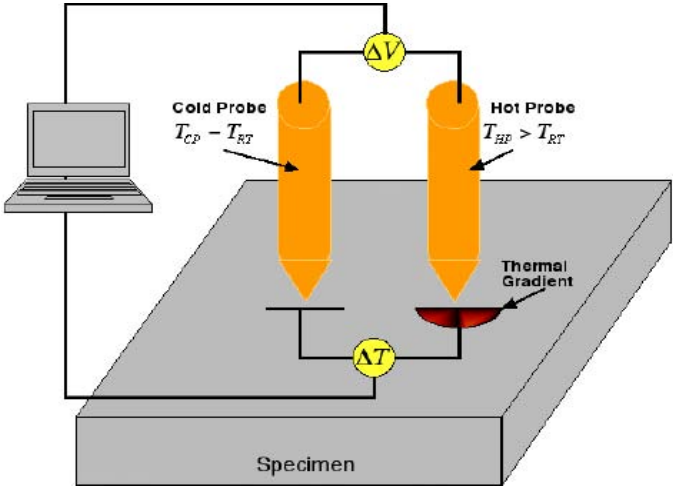


QUESTION:

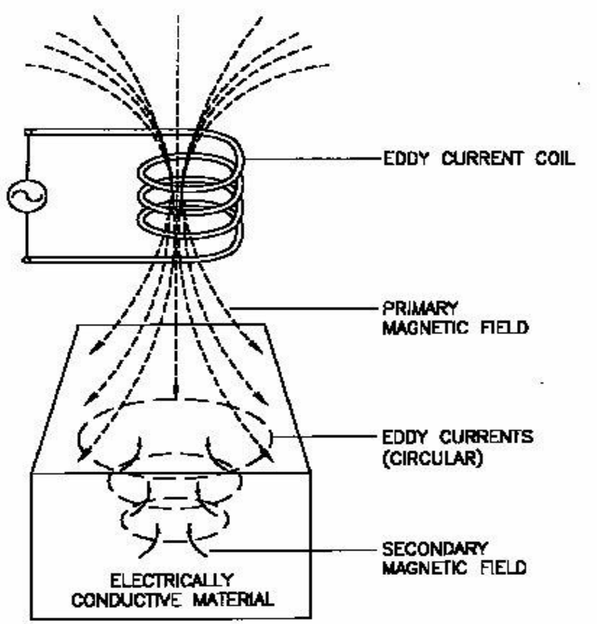
If you can calculate e/a, why can't you measure it?



Electronic Property Measurement Tools



- Thermoelectric Power
  - Contact Technique



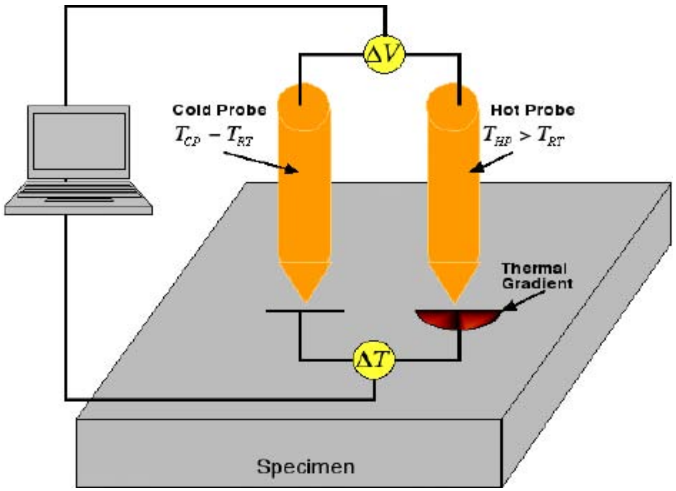
- Low Frequency Impedance Measurements
  - Non-Contact Technique

Quantum Mechanical Principle of Thermoelectric Power

$$S = \left(\pm \frac{k}{e}\right)(27.1)\left(r + \frac{3}{2}\right)\left(\frac{m_e}{h^2}\right)\left(kTn^{\left(-\frac{2}{3}\right)}\right)$$

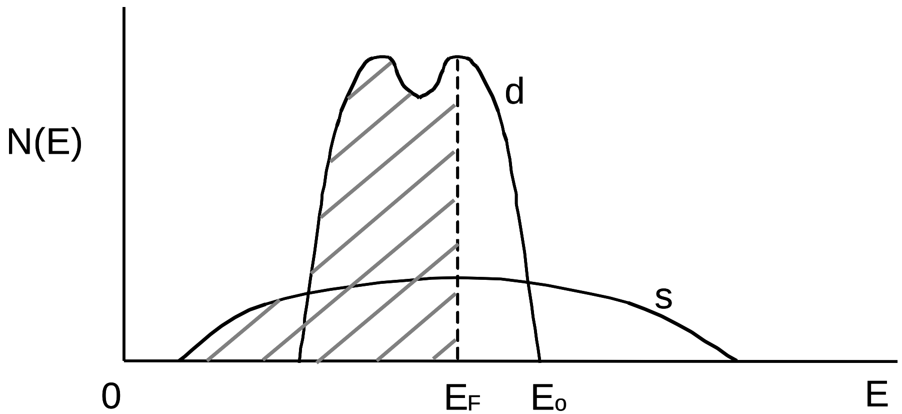
$$S = S(n, m_e, r)$$

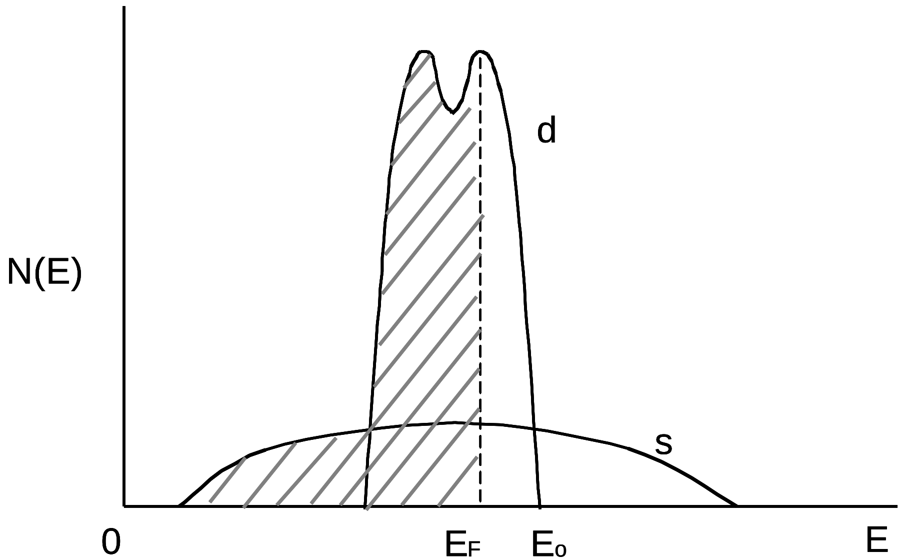
- S Thermoelectric power
- r Scattering parameter
- h Planck constant
- k Boltzmann's constant
- n Free electron concentration
- m_e Effective mass (m*)



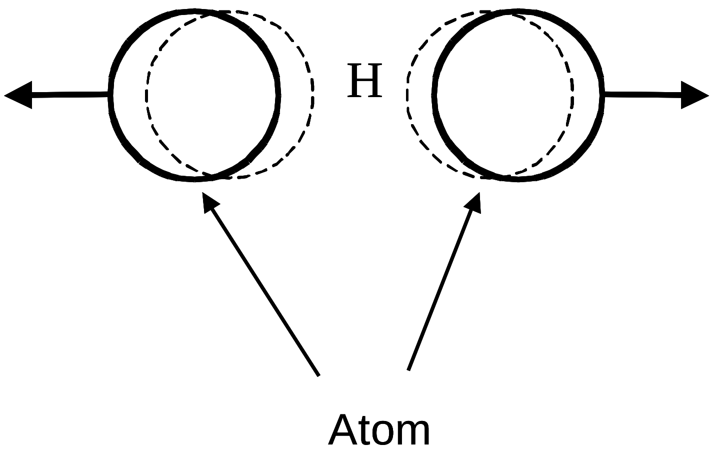
$$m_e = \frac{\hbar^2}{\left(d^2E \big/ dk^2\right)}$$

Electronic Nature of Hydrogen



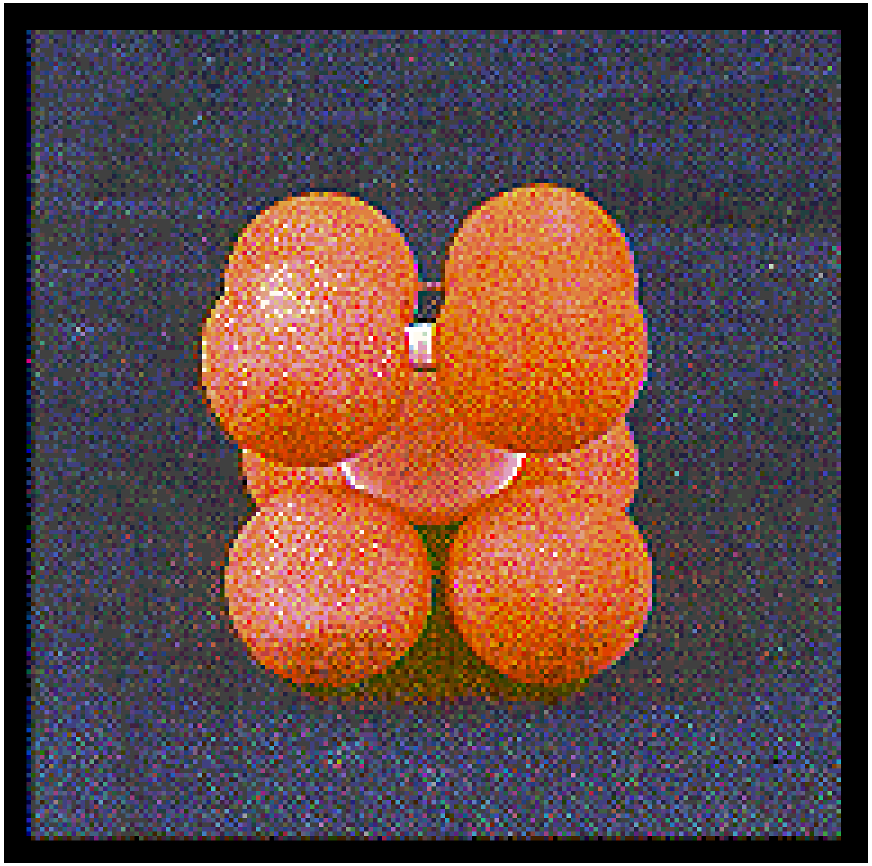


$$E_F = \frac{\hbar^2 k^2}{2m_e}$$



$$m_e \propto \frac{1}{\left(d^2E \big/ dk^2\right)}$$

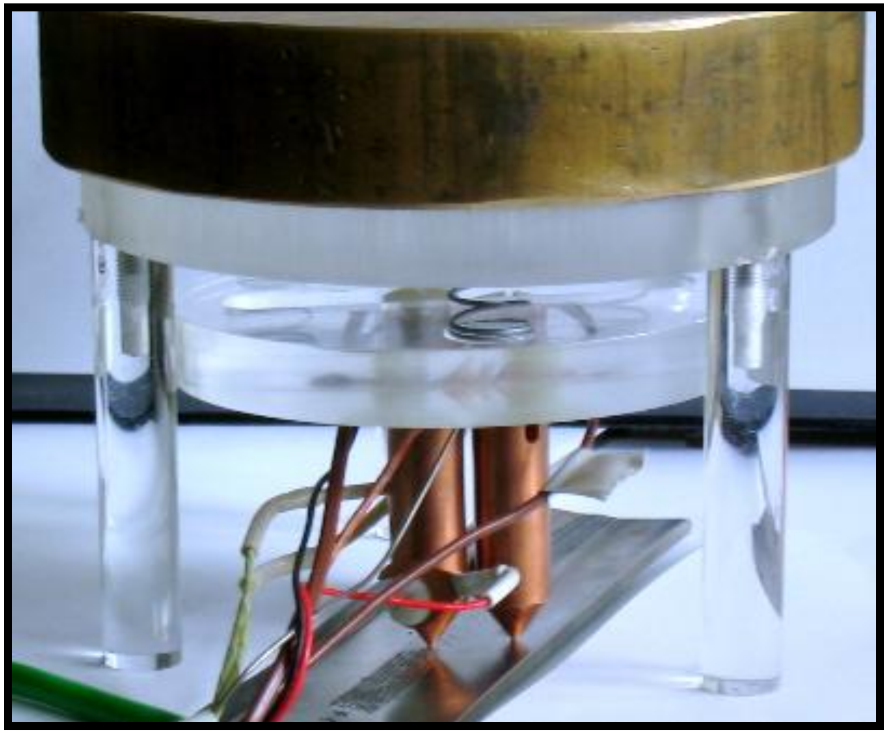
Hydrogen in BCC Interstitial Sites

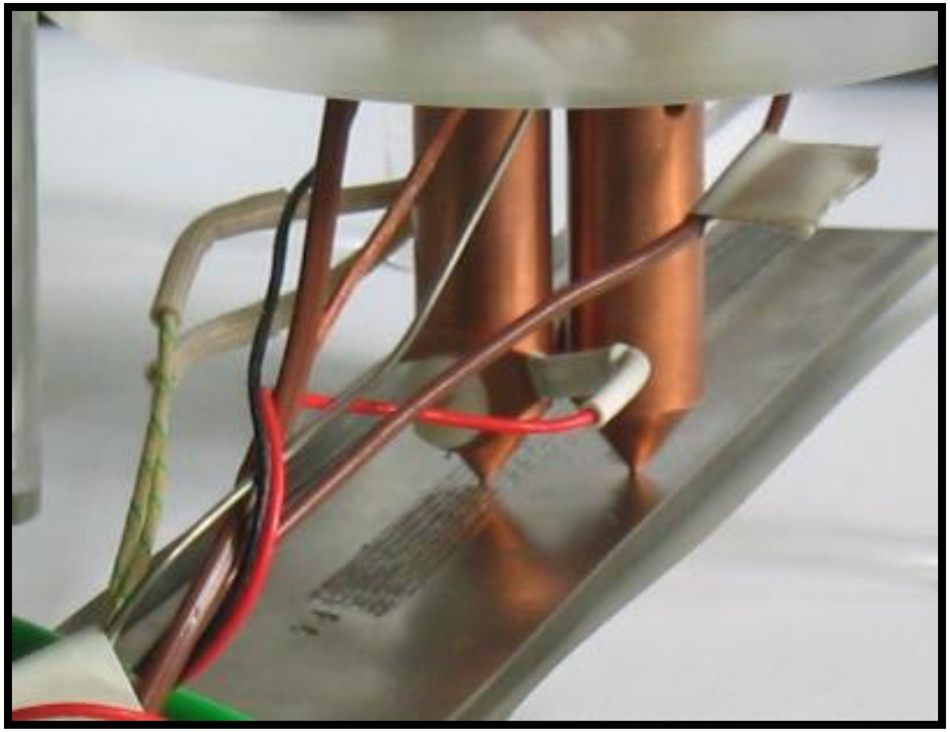


	Tetra-hedral	Octa-hedral
BCC-Iron Interstitial Hole Size	0.36 Å	0.19 Å
H-Filled Interstitial Hole Size	0.87 Å	0.66 Å

Ref:[Fukai, 1993]

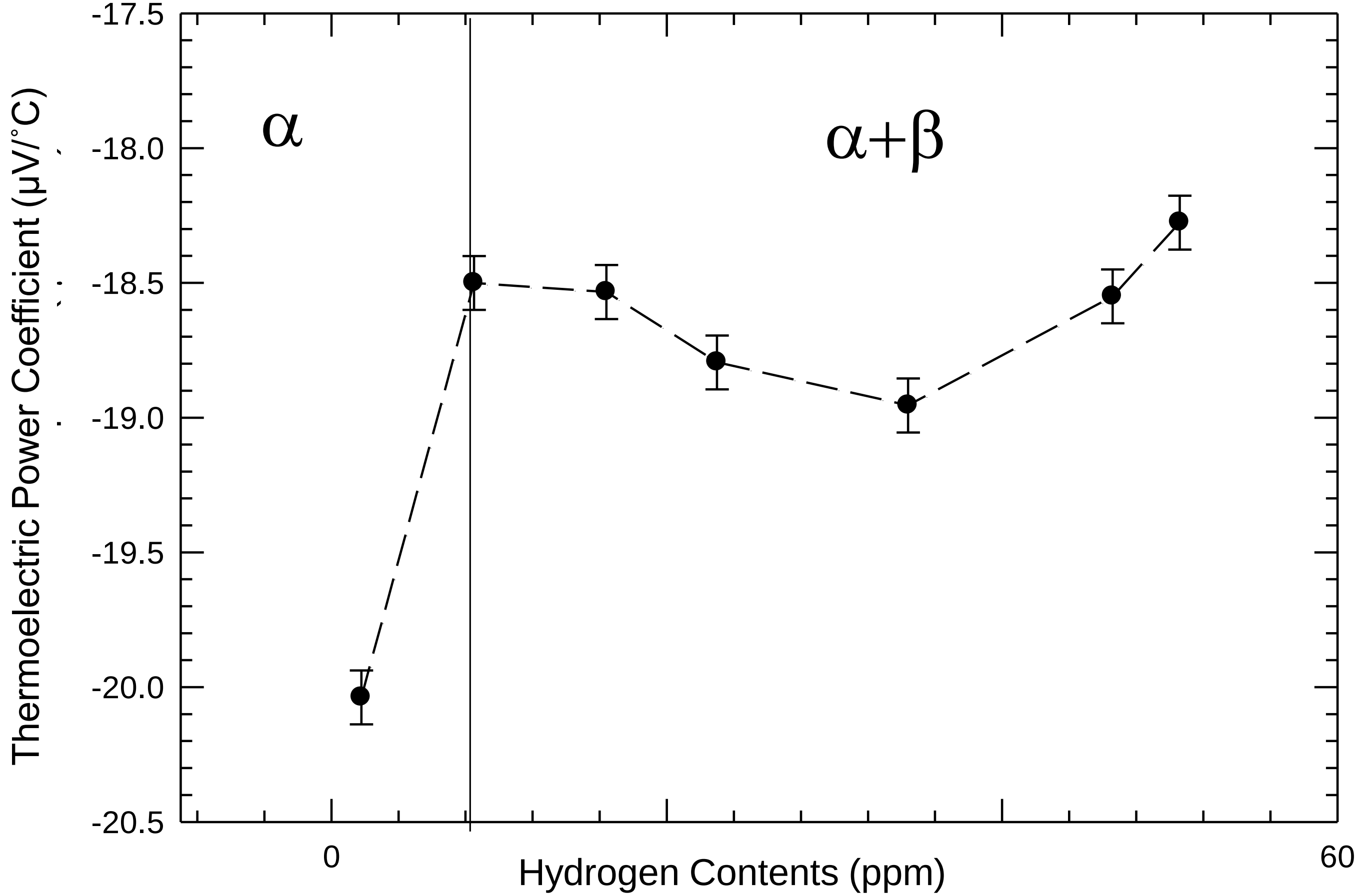
Thermoelectric Power Surface Probe





Contact diameter of probe tip: 0.015 inches (381 μ)

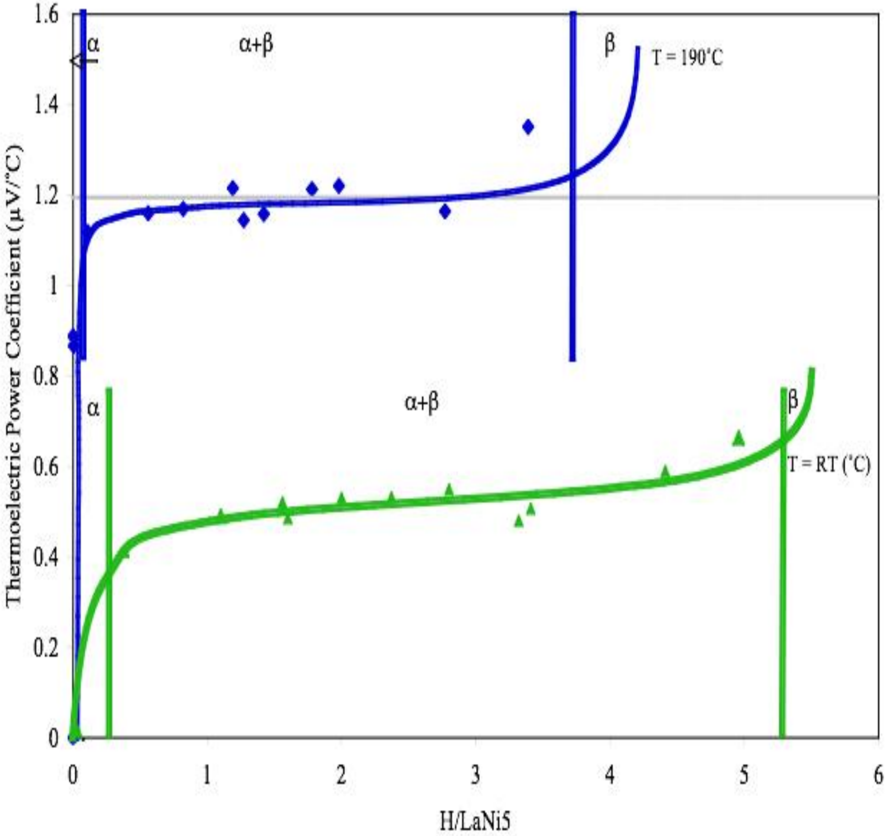
Thermoelectric Power as a Function of Hydrogen in Monel K-500

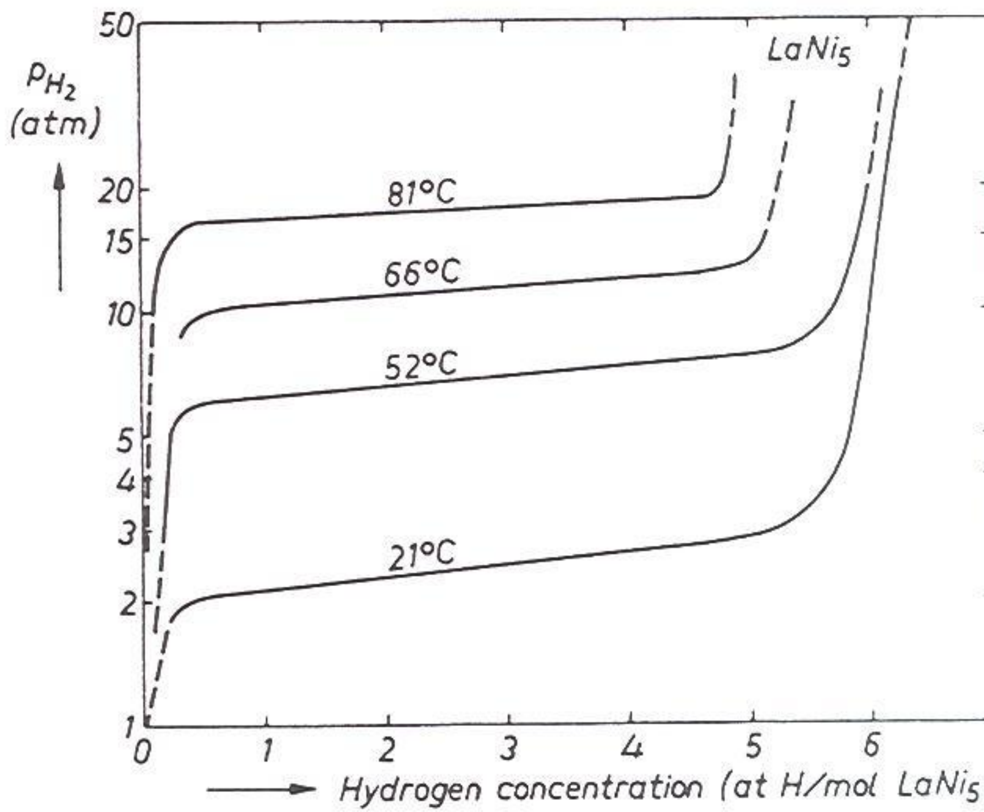


Hydrogen contents (ppm)

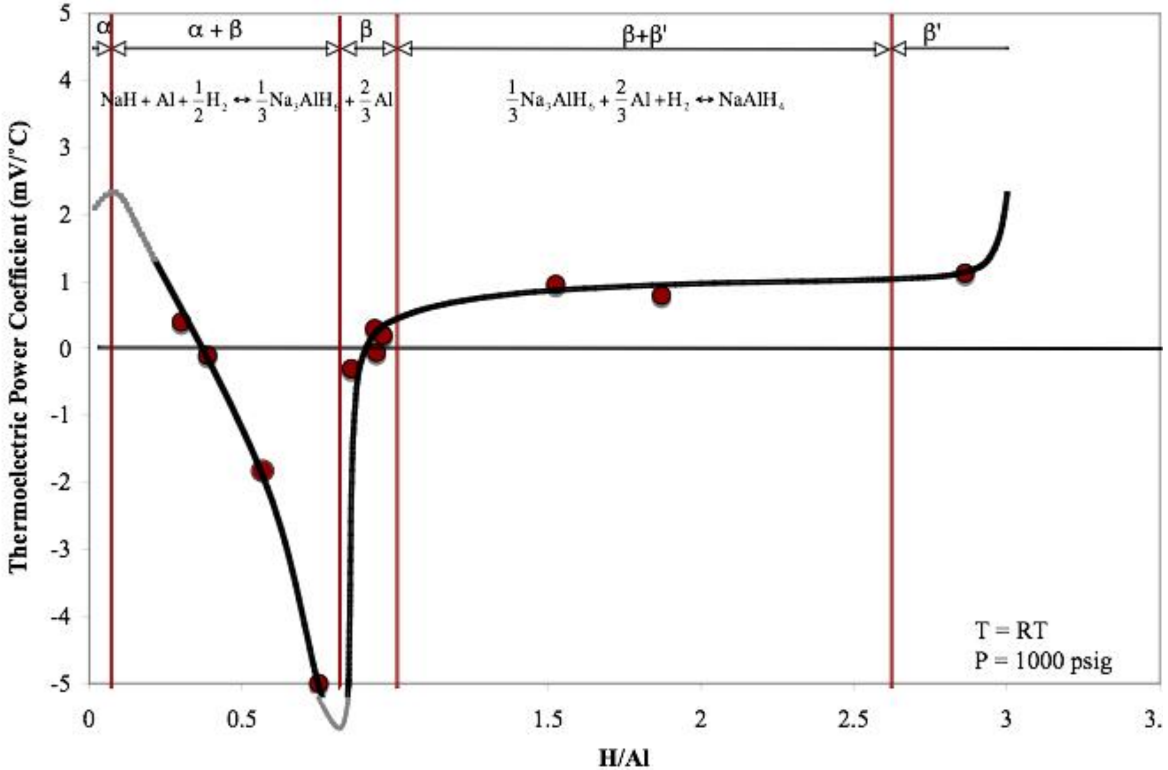
Park *et. al.* International Proceeding of NACE International 2004, Paper No 04265

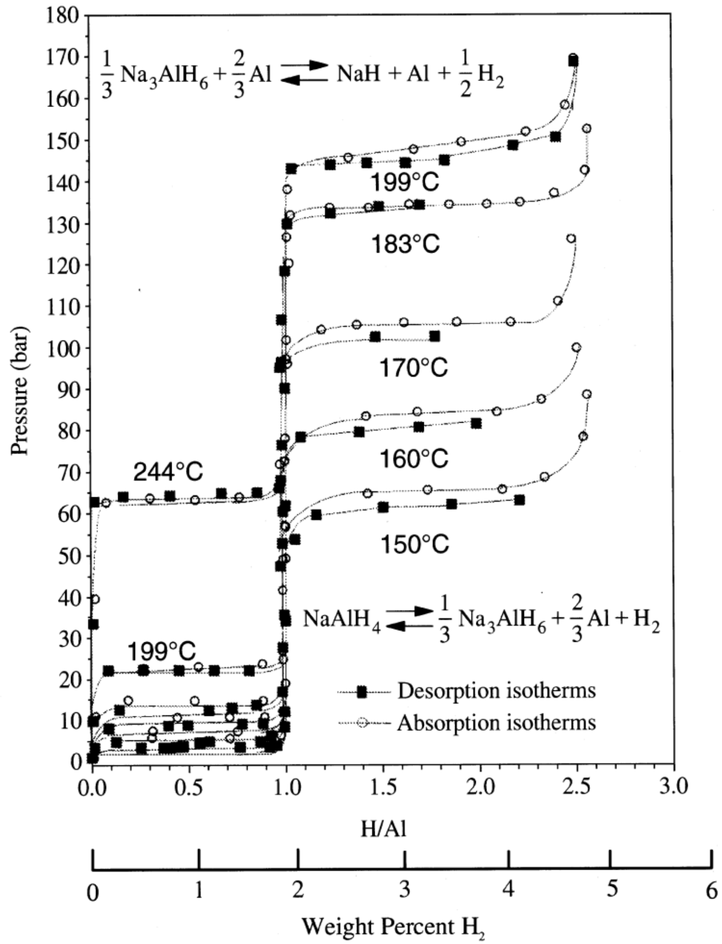
Thermoelectric Power as a Function of H/LaNi$_5$





Thermoelectric Power as a Function of H/Al

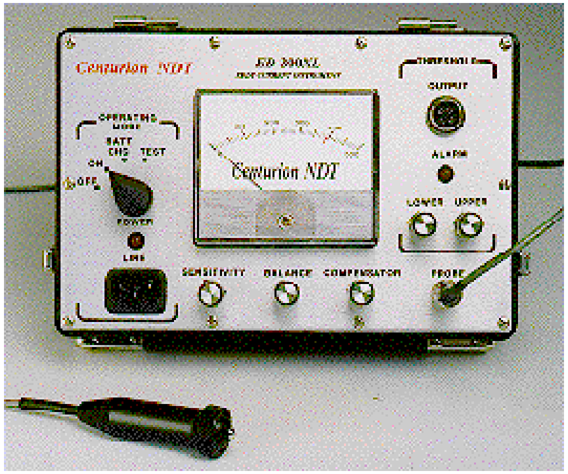




Bogdanovic et al., 2000

Eddy Current Analysis

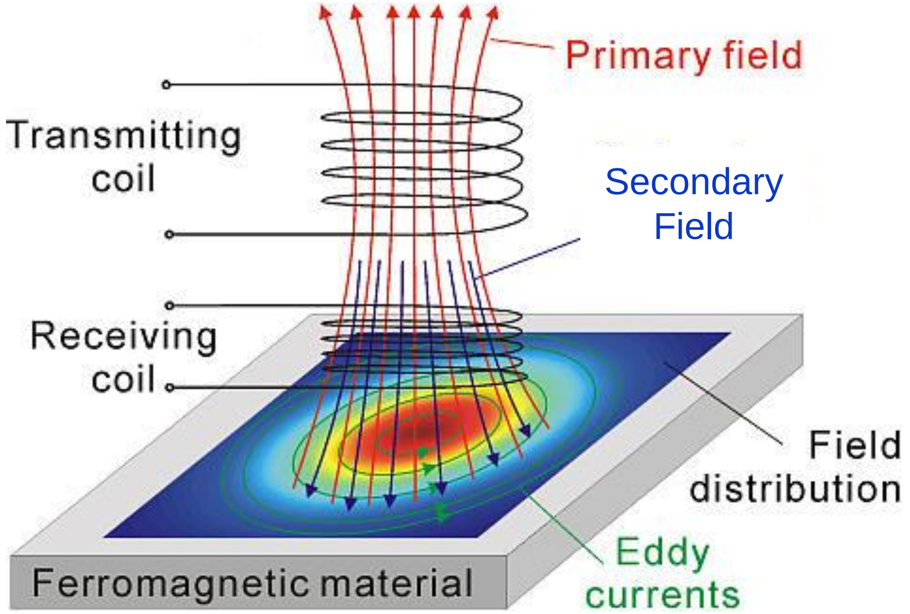
- Eddy current non-destructively measure:
  - Plate and coating thickness
  - Conductivity
  - Differences in composition, microstructure, and properties
  - Cracks, defect, flaws
  - Hardness and physical conditions



Eddy Current Analysis

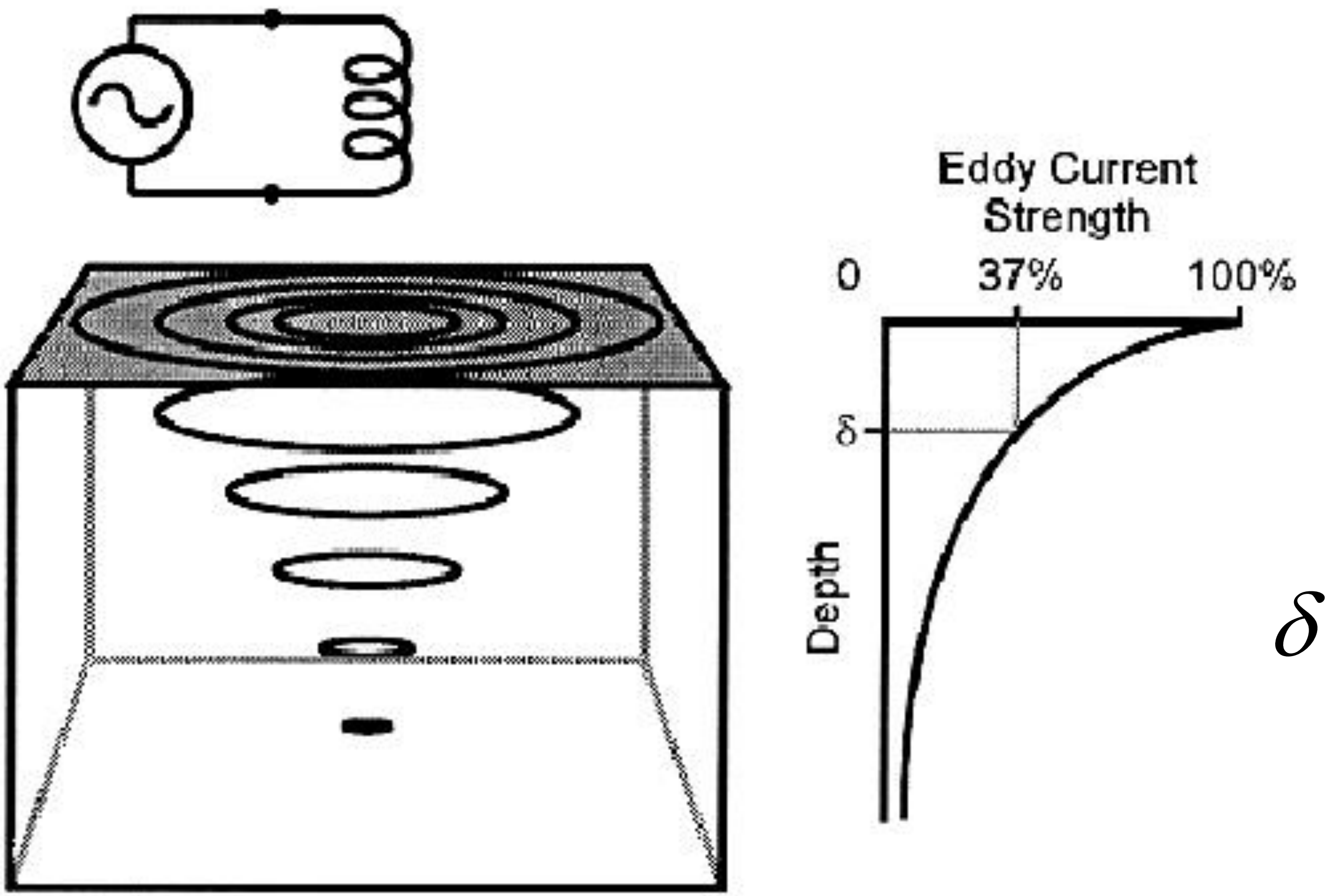
- Eddy Currents
  - Spread out into the specimen
  - Will naturally be constrained by the specimen boundaries
  - Circulating currents produce their own secondary flux, Φ_S
  - This secondary flux is in opposition to Φ_P
- The coil now senses an equilibrium flux:

$$\Phi_E = \Phi_P - \Phi_S$$



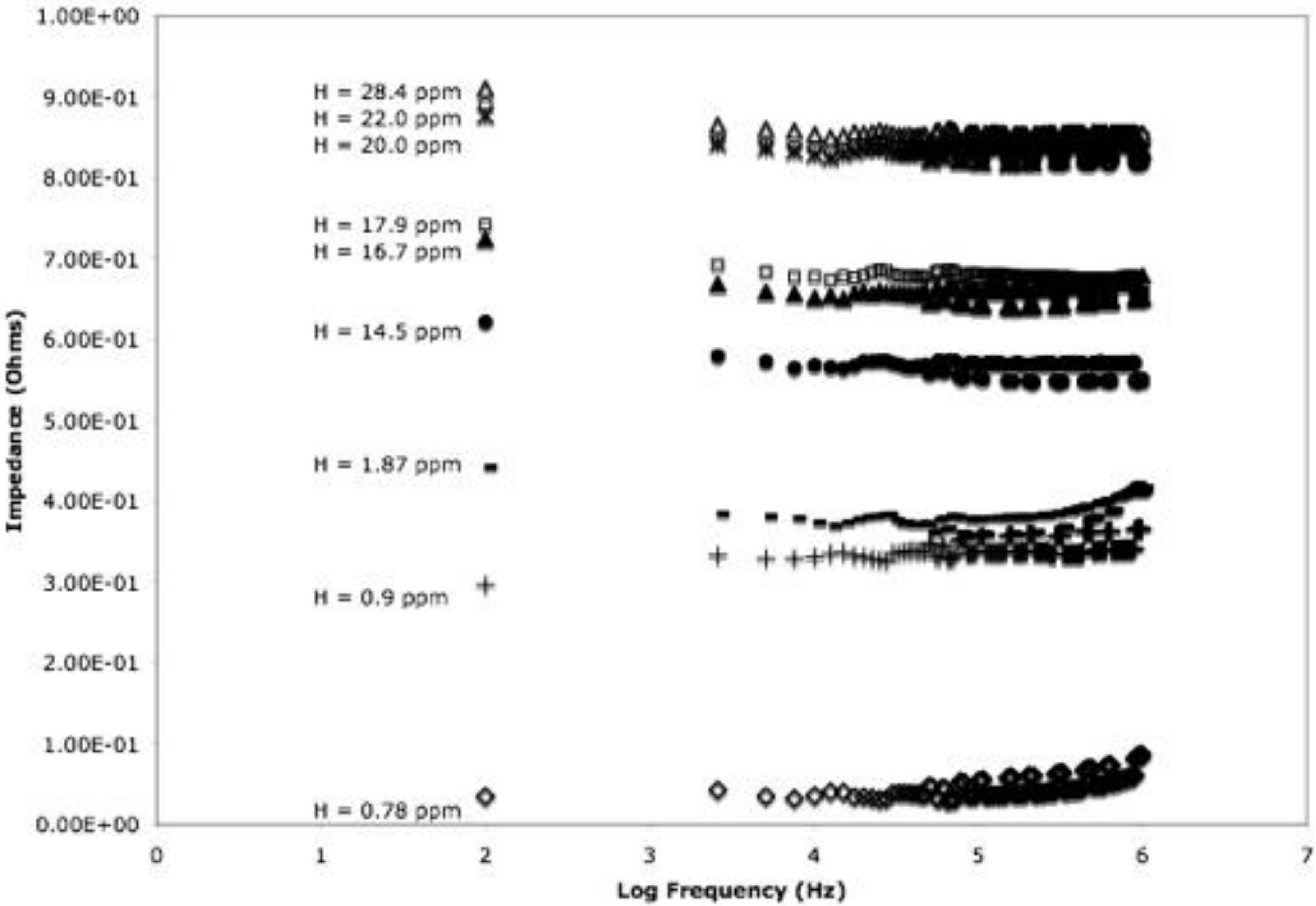
Klümper-Westkamp et al., 2003

Eddy Current Theory

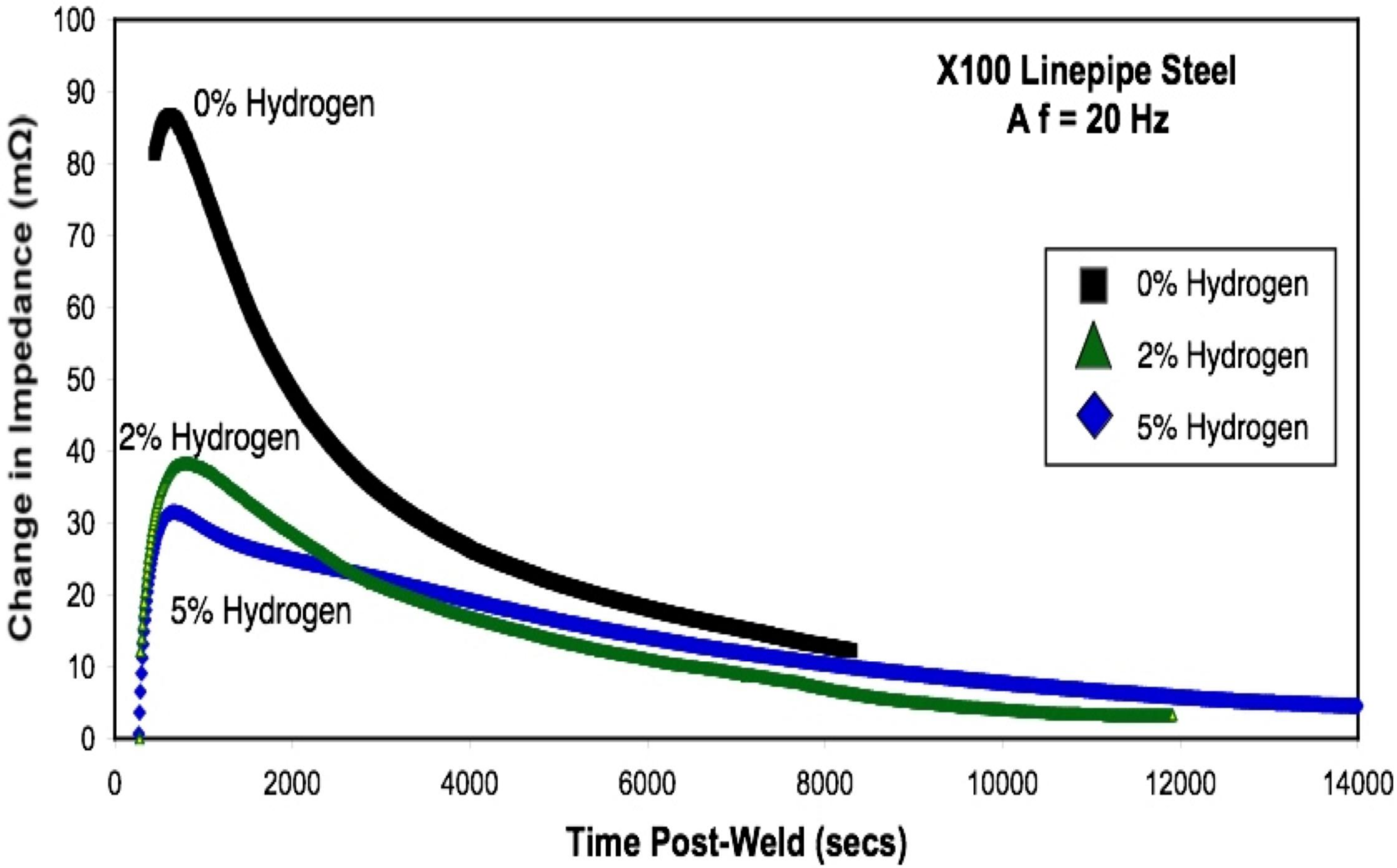


$$\delta \propto \frac{1}{f^{1/2}}$$

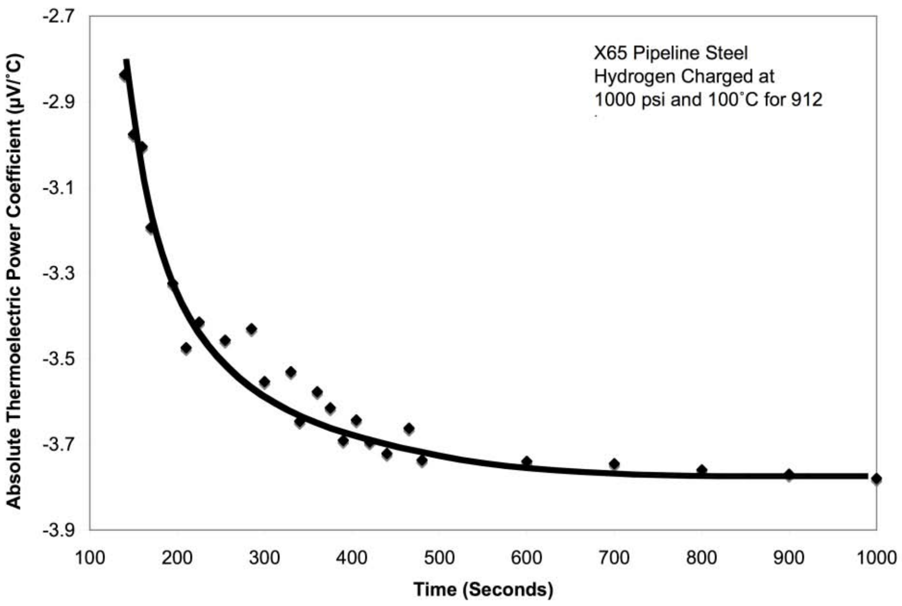
Low Frequency Impedance Measurements

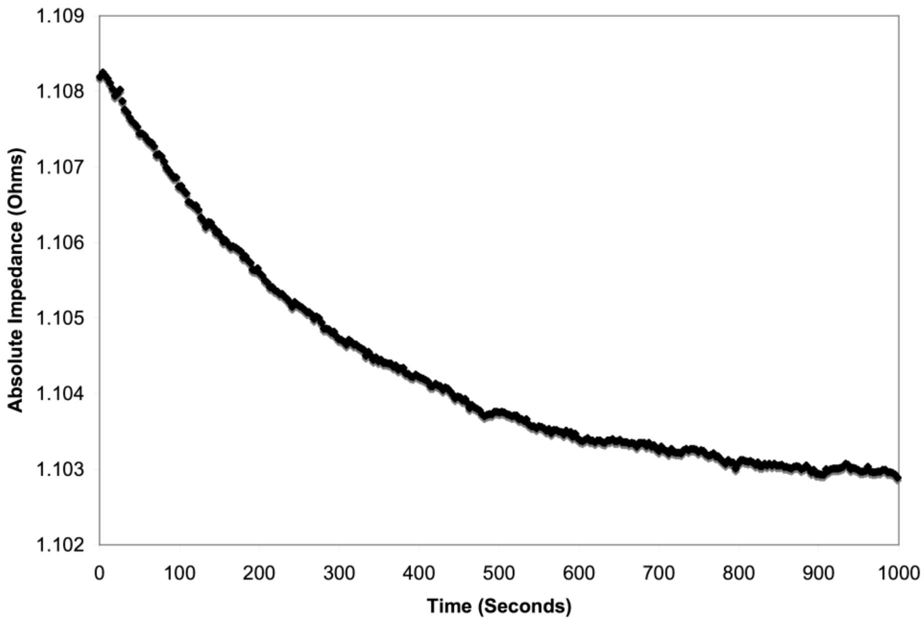


Impedance as a Function of Time as Hydrogen Diffuses out of Steel Weld Metal



Thermoelectric Power and Impedance as a Function of Time





Additional Non-Destructive Tools

- **Electronic**
  - Conductivity
  - TEP
  - Hall Effect
- **Magnetic**
  - Susceptibility
- **Electromagnetic**
  - Eddy Current
  - EM-Acoustic -> Barkhausen Noise
  - Electromagnetic Radiation (X-ray, gamma, and tera)
- **Elastic**
  - Acoustic Emission – Kaiser Effect
- **Thermal Analysis**
  - Infrared

Summary

- Both thermoelectric power and low frequency impedance measurements successfully provide real-time, non-destructive, hydrogen content measurements in advanced materials.

Acknowledgements

- DOT-PHMSA
- CSM-Dept. of Physics
- Agilent Technologies
- Holland Consulting
- TMR Exploration
- Blade Energy

Diffusion Coefficient of Hydrogen in Steel

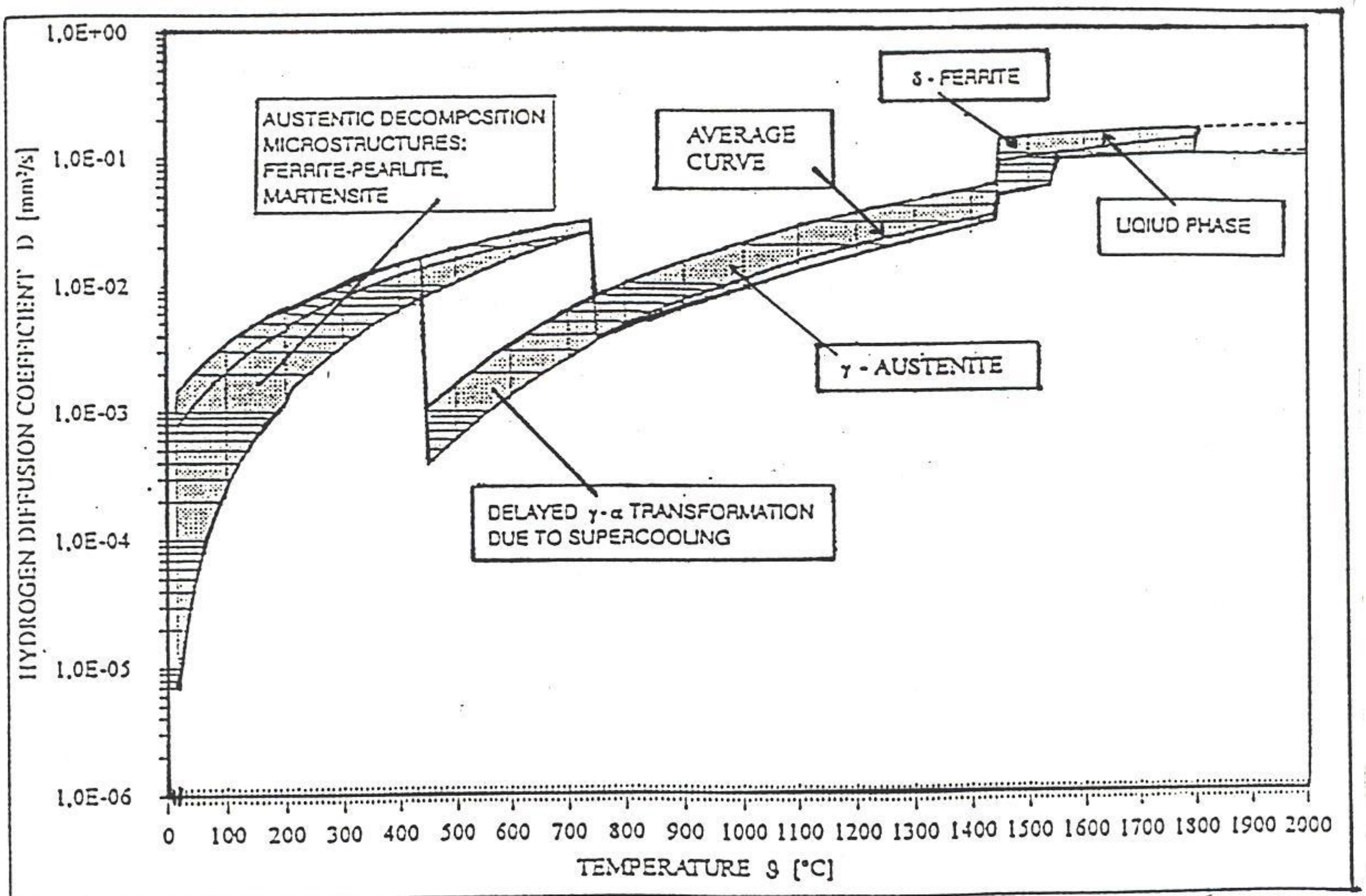


Fig. 13: Scatterband for hydrogen diffusion coefficients in micro alloyed and low carbon structural steels

Current Methods for Hydrogen Measurement

- Laser Ablation/Gas Chromatography
- Laser Ablation/Mass Spectrometer
- Electrochemical
- Opto-electronic diffusible hydrogen sensor
- AWS Volumetric Displacement